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Cyanine Borate Salts That Form Penetrated Ion Pairs in Benzene Solution: Synthesis, Properties, and Structure

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A series of cyanine borate salts were prepared and studied by laser spectroscopy, fluorescence spectroscopy, NMR spectral methods, and computer modeling. Analysis of the chemical, physical, and spectral properties of these salts shows that, in benzene solution, they form penetrated ion pairs. The center-to-center distance between the ions is less than the sum of the individual ionic radii. We call such structures penetrated ion pairs. Penetration affects the properties of the cyanine dyes in unique ways that are described.

Some cyanine cations[1,2] form salts with tetraarylborate anions that are soluble in hydrocarbon solvents such as benzene. At low concentration, these salts exist as ion pairs with unusual structures and properties. In particular, since borate anions have cavities with appropriate dimensions, the cyanine cations can penetrate within their perimeter. The driving force for penetration is minimization of energy through Coulombic attraction, which is an especially strong impetus in solvents of low dielectric constant such as benzene.

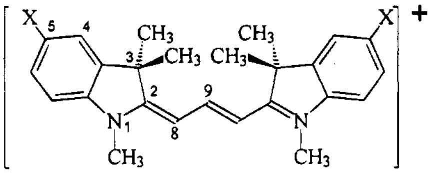
We prepared substituted indocarbocyanines having either electron-withdrawing or -donating substituents in the 5 and 5′ positions and a series of substituted tetraarylborates. The structures of the arylborates was varied systematically to control their "size". Computer modeling, spectroscopic measurements, and examination of reactivity reveals a penetrated ion pair structure for cyanine borate salts in benzene solutions. The size of the borate controls many of the properties of the ion pair.

Results

The Cyanine Cations. The 1,3,3,1′,3′,3′-hexamethylindocarbocyanine dyes (X-Cy) examined in this work are shown in Chart 1. Their synthesis from *para*-substituted anilines yields structures with substituents at the 5 and 5′-positions. These substituents affect many of the properties of the cyanine dyes.

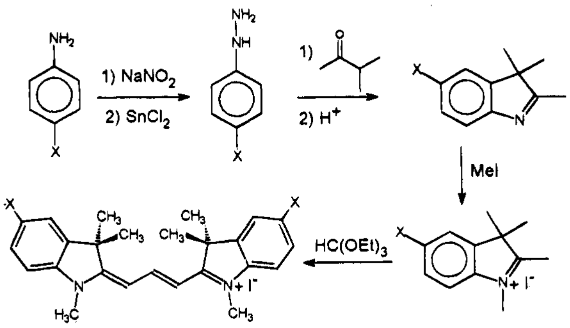
Synthesis of Cyanine Dyes. A general route for synthesis of cyanine dyes is shown in Scheme 1. A substituted hydrazine, formed by reduction of a diazonium salt, is combined with methyl isopropyl ketone in the Fischer indole synthesis. Methylation with methyl iodide gives substituted indolinium salts which react with triethyl orthoformate to yield the cyanine dyes as their iodide salts. This route works satisfactorily for all of the cyanine dyes shown in Scheme 1 except the (trifluoromethyl)sulfonyl substituted example. In this case, the indolinium iodide was prepared with a trifluoromethyl thiol substituent by the route described, and subsequent oxidation gives the (trifluoromethyl)sulfonyl groups.

Chart 1. Substituted Cyanine Dyes

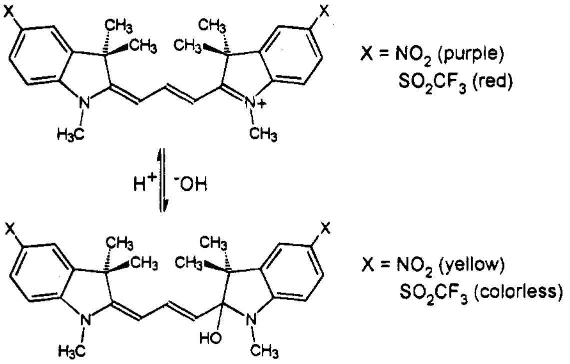


X = OMe, Me, H, CF_3, NO_2, SO_2CF_3

Scheme 1. General Synthesis of Cyanines from Substituted Anilines



Scheme 2. Acid and Base Dependence of Cyanine and Pseudobase



In the course of this work, it was necessary to exchange the iodide counterion generated in the synthesis of the cyanine for another anion. Dyes substituted with strong electron-withdrawing groups react with potassium hydroxide to give a pseudobase (Scheme 2). The cyanine is re-formed from the pseudobase by addition of acid. The process is completely reversible and is useful for exchange of anions.

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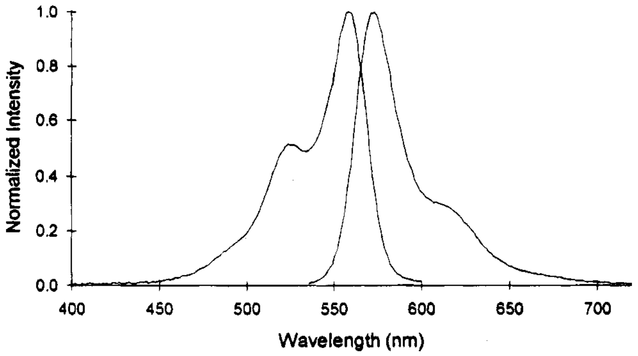

Figure 1. Absorption and emission spectra of H-Cy in benzene.

Table 1. Photophysical and Electrochemical Data for Cyanines

X	$\lambda_{abs}{}^a$ (nm)	λ_{em} (nm)	$E_{red}{}^b$ (V)	E_{00} (eV)	τ (ps)	Φ_{fl} (%)	k_{fl} (s−1)
OMe	583	600	−1.04	2.10	310	3.3	1.1×10^8
Me	570	583	−1.01	2.15	300	4.7	1.6×10^8
H	558	572	-0.96^c	2.20	250	4.7	1.9×10^8
CF_3	556	570	−0.74	2.21	290	6.2	2.1×10^8
NO_2	581	594	−0.56	2.11	710^d	13^d	$1.8 \times 10^{8\,d}$
SO_2CF_3	568	580	−0.50	2.16	510	10	2.0×10^8

[a] All values measured in benzene with PF_6 counterion unless otherwise noted. [b] vs SCE in acetonitrile and referenced to H-Cy. [c] Value taken from ref[40] for 1,1′-diethyl-3,3,3′,3′-tetramethylindocarbocyanine. [d] Measured for the *dl*-10-camphor sulfonate anion in benzene.

Spectroscopic and Physical Properties of Cyanines. Typical absorption and emission spectra of cyanines are shown in Figure 1. Critically, these dyes absorb strongly at 532 nm, which is the second harmonic of neodymium:YAG lasers.[3] This permits examination of their photophysical processes and electron transfer reactions on a picosecond time scale.

In order to study electron transfer reactions of cyanines, their reduction potential (E_{red}), singlet lifetime (τ_S), and the excited state singlet energy (E_{00}) must be measured. These data, along with the absorption and emission maxima, the fluorescence quantum yields, and the fluorescence rate constants are gathered in Table 1. E_{00} of the cyanine cations is taken as the point where the normalized absorption and emission spectra overlap. E_{red} was measured in acetonitrile solution using cyclic voltammetry.[4] Not surprisingly, the reduction potentials of the cyanine are correlated with the Hammet σ_p values of their substituents. A plot of E_{red} vs σ_p is shown in Figure 2 along with the best fit of the data to a quadratic equation. The relationship is empirical, but useful for predicting the reduction potential to within ±0.02 V.

2. The Tetraarylborates. Tetraarylborates (Ar_4B^-)[5] have been used as components in lithography,[6] reagents for the determination of Na^+ and Cs^+,[7] and as constituents in antiperspirants.[8] Borates with three aryl groups and one alkyl group are useful as commercial photoinitiators of polymerization.[9] Tetraarylborates are well suited for the study of electron transfer in ion pairs. They have oxidation potentials high enough to make them stable compounds, but low enough to participate in photointiated electron transfer with cyanine dyes. Many substitution patterns are possible, since the borates may be composed of up to four different aryl groups. This variety of structure allows the systematic examination of the chemical and physical properties of cyanine borate ion pairs.

The borates utilized in this work are listed in Table 2. The majority are tetraarylborates with alkyl substituents *para* to the boron atom. Four borates, TRPB, DBB, 4OTB, and 3OTB, contain "bulky" substituents on the aryl groups. Two series of tolyl "mixed borates" were examined. Mixed borates are defined as borates with two or more different aryl groups bound to the boron atom. The mixed borates investigated in this work have tolyl and phenyl groups that form an *ortho* and a *para* series.

Synthesis of Tetraarylborates. The symmetrical tetraarylborates salts were generally prepared in yields of 60−70% from arylmagnesium bromides and tetramethyammonium tetrafluoroborate as shown in eq 1.

$$\mathrm{ArBr} \xrightarrow[\text{(3) (Me)}_4\text{NCl}]{\text{(1) Mg, (2) NaBF}_4} \mathrm{Me_4N^+(Ar)_4B^-} \tag{1}$$

$$\mathrm{BCl_2(NEt)_2} \xrightarrow[\text{(2) BCl}_3]{\text{(1) PhMgBr}} \mathrm{(Ph)_2BCl} \tag{2}$$

This approach was not satisfactory for the preparation of tetrakis(3,5-di-*tert*-butylphenyl)borate which was prepared by addition of the aryllithium reagent to boron trichloride. The mixed borates were prepared from (chlorophenyl)boranes. Borates with one tolyl group were prepared from triphenylborane and tolyllithium. Chlorodiphenylborane was added to tolylmagnesium bromide to give borates with two tolyl groups, eq 2. Borates with three tolyl groups were prepared from dichlorophenylborane.

Oxidation Potentials of Borate Anions. Systematic evaluation of electron transfer reactions of cyanine borate ion pairs requires measurement of the borate oxidation potentials (E_{ox}). Unfortunately, due to the extremely short lifetime of the boranyl radical (the one-electron oxidized form of the borate), E_{ox} cannot be determined by conventional electrochemical techniques. We developed a reliable kinetic method based on the Marcus theory of electron transfer for determination of E_{ox} of tetraarylborates.[10] The result of applications of this method to the borates of this work are included in Table 2.

3. Cyanine Borates. The structures of the cyanine borate ion pair in benzene solution were examined by chemical, physical, and computational procedures. Conductivity experiments show that cyanine borates form contact ion pairs in nonpolar solvents. Extrapolation of dissociation constants measured in a range of solvents yields a dissociation constant in benzene solution (ϵ =

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(3) Sauerwein, B. Ph.D. Thesis, University of Illinois at Urbana−Champaign, 1992.

(4) The working electrode used was a 50 μm (diameter) gold microelectrode, the counter electrode was platinum, and the reference electrode was Ag/AgCl. All measurements were referenced internally to ferrocene which was added to the solution.

(5) The term borate is also used for compounds derived from boric acid. The Nomenclature of Boron Compounds. *Inorg. Chem.* **1968**, *7*, 1945. Moore, C. E.; Vandenberg, J. T. *CRC Crit. Rev. in Anal. Chem. Tetraarylborates* **1971**, *2*(1), 1.

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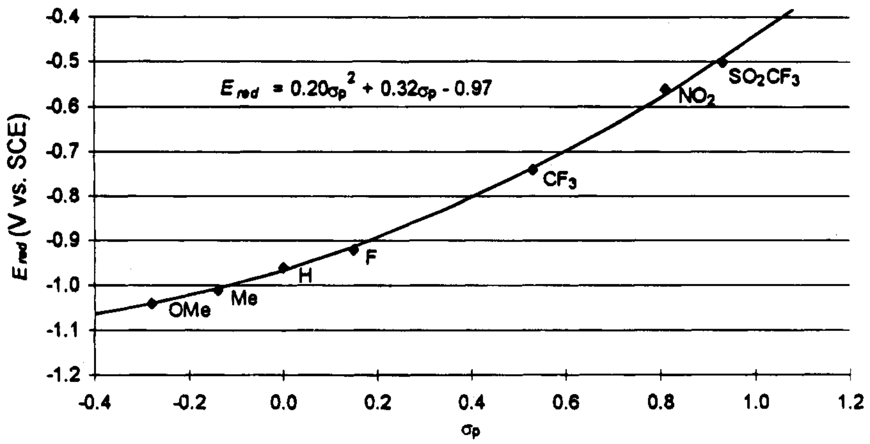

Figure 2. Relationship between Hammet σ_p values and reduction potentials of cyanines.

Table 2. Tetraarylborates

abbreviation	substitutions [a]	E_{00} vs SCE
PHB	R_1-_4 = phenyl	0.76
BPB	R_1-_4 = 4-biphenyl[b]	
MBPB	R_1-_4 = 4′-methyl-4-biphenyl[b]	
BBPB	R_1-_4 = 4′-*tert*-butyl-4-biphenyl[b]	
DMB	R_1-_4 = 3,5-dimethylphenyl	0.56
DBB	R_1-_4 = 3,5-di-*tert*-butylphenyl	
CHPB[d]	R_1-_4 = 4-cyclohexyl[c]	
TRPB[d]	R_1-_4 = 4-triptycenyl[c]	
FLB	R_1-_4 = 4-flourophenyl	0.93
MOB	R_1-_4 = 4-methoxyphenyl	0.36
POB	R_1-_4 = 4−*iso*-propoxyphenyl	0.33
4PTB	R_1-_4 = 4-methylphenyl	0.55
TBB	R_1-_4 = 4−*tert*-butylphenyl	
ADB	R_1-_4 = 4-adamantylphenyl[c]	
3PTB	R_1-_3 = 4-methylphenyl, R_4 = phenyl	0.59
2PTB	R_1-_2 = 4-methylphenyl, R_3-_4 = phenyl	0.63
1PTB	R_1 = 4-methylphenyl, R_2-_4 = phenyl	0.68
4OTB	R_1-_4 = 2-methylphenyl	0.71
3OTB	R_1-_3 = 2-methylphenyl, R_4 = phenyl	0.71[d]
2OTB	R_1-_2 = 2-methylphenyl, R_3-_4 = phenyl	0.71[d]
1OTB	R_1 = 2-methylphenyl, R_2-_4 = phenyl	0.75

[a] Borates are of the general type $^-BR_1R_2R_3R_4$, where the 1-position is *ipso* to the boron and the 4-position is *para* where the R groups are benzene rings. [b] The carbons where the two phenyl rings are attached are the 1- and 1′-positions and so the 4- and 4′-positions are *para* to these carbons. [c] The group is attached at the bridgehead carbon. [d] The 2-methyl groups hinder approach to the boron atom.

Table 3. Electron Transfer Rates in Borates of Various Sizes

R in $^-B(Ph\text{-}R)_4$[a]	radius of borate	k_{et} (s^{-1})
CH_3	6.5	3.1×10^{11}
$C(CH_3)_3$	7.8	4.0×10^{11}
adamantyl[b]	9.8	4.5×10^{11}
Ph	9.9	1.2×10^{11}
4-CH_3Ph	10.7	1.6×10^{11}
4-$C(CH_3)_3$Ph	12.1	2.2×10^{11}

[a] R is *para* to the boron. [b] The adamantyl group is attached at the bridgehead carbon atom.

2.28 D) of ca. 9 × 10^{-17} M[11] At the concentrations of relevance for this work, in benzene solution, the cyanine borates exist essentially exclusively as contact ion pairs.

Photoinduced Electron Transfer Reactions of Cyanine Borates. The excited singlet state of cyanine dyes undergo several processes that generally do not involve the counterion. The major deactivation paths of the excited cyanine are bond rotation ($k_{rot.}$), which reforms the original *all-trans*-cyanine or leads to a metastable mono *cis*-isomer, and fluorescence (k_{fl}).[11] Intersystem crossing[12] (k_{isc}), usually is not observed at room temperature without the aid of heavy atoms[13,14] (the nitro-substituted cyanine is an exception[15]). When the cyanine has a tetraarylborate counterion, electron transfer from the borate to the excited cyanine to give a radical pair (k_{et}) is an important process. These reactions are outlined in Scheme 3.

Scheme 3

$$[Cy^+][X^-] \xrightarrow{h\nu} [Cy^+]^*[X^-]$$

$$[Cy^+]^*[X^-] \xrightarrow{k_{fl}} [Cy^+][X^-]$$

$$[Cy^+]^*[X^-] \xrightarrow{k_{rot.}} [isoCy^+][X^-]$$

$$[Cy^+]^*[X^-] \xrightarrow[{[X^-] = Ar_4B^-}]{k_{et}} [Cy^\bullet][X^\bullet]$$

The rate constant of an electron transfer reaction is a sensitive measure of orbital overlap which is normally related to the distance (r_{DA}) between the donor and acceptor. Since ions are usually considered to be impenetrable hard spheres, the radius of the borate anion should control r_{DA}. Consequently, substituents on the *para* position of a tetraarylborate, which increase its radius, might dramatically slow k_{et}. This hypothesis was tested with a series of substituted phenyl- and biphenylylborates.

The data in Table 3 show a series of tetraarylborates, their radii estimated by molecular mechanics calculations, and k_{et} measured by time-resolved absorption and fluorescence spectroscopy.[16] As the structure of the borate is changed, the assigned radius increases by nearly a factor of 2 from 6.5 to 12.1 Å, but k_{et} remains

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[11] Chaterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329.

[12] The triplet could not be observed for this cyanine in our experiments. The rate is an estimation for a similar cyanine with oxygen atoms replacing the two *gem*-dimethyl groups: Chibisov, A. K. *J. Photochem.* **1976/77**, *6*, 199.

[13] Kuz'min, V. A.; Darmanyan, A. P.; Shirokova, V. I.; Al'perovich, M. A.; Levkoev, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim., Engl. Trans.* **1978**, 501.

[14] Sauerwein, B.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *95*, 1903.

[15] The evidence for the NO_2-Cy intersystem crossing is the fact that ca. 40% of the bleaching of the ground state remains after 10 ns. No other absorptions are seen in the transient absorption spectrum including the lack of a peak where the expected *cis*-isomer should appear. The existence of a significant intersystem crossing pathway does not affect the electron transfer studies.

Table 4. Electron Transfer Rates for X-Cy with "Bulky Borates"

X/borate	$B-C_{cent}$ (Å)	est ΔG_{et} (eV)	$k_{et} \times 10^9$ (s^{-1})
H/3OTB	5.8	−0.48	110
Me/3OTB	5.8	−0.38	26
MeO/3OTB	5.8	−0.30	5.3
H/4OTB	6.2	−0.50	130
Me/4OTB	6.2	−0.40	40
MeO/4OTB	6.2	−0.32	5.7
Me/DBB	6.0	−0.52	180
MeO/DBB	6.0	−0.44	220

Table 5. Electron Transfer Rates for X-Cy with "Normal Borates"

X-Cy/ borate	ΔG_{et} (eV)	k_{et} (s^{-1})	X/borate	ΔG_{et} (eV)	k_{et} (s^{-1})
H/FPB	−0.24	4.7×10^9	MeO/PHB	−0.23	4.0×10^9
H/PHB	−0.41	4.3×10^{10}	MeO/1OTB	−0.24	4.7×10^9
H/1OTB	−0.42	7.7×10^{10}	MeO/2OTB	−0.28	5.5×10^9
H/2OTB	−0.46	9.9×10^{10}	MeO/1PTB	−0.31	6.9×10^9
H/1PTB	−0.49	9.9×10^{10}	MeO/2PTB	−0.36	1.2×10^{10}
H/2PTB	−0.54	1.8×10^{11}	MeO/3PTB	−0.40	2.2×10^{10}
H/3PTB	−0.58	3.0×10^{11}	MeO/DMB	−0.43	6.8×10^{10}
H/DMB	−0.61	9.2×10^{11}	MeO/4PTB	−0.44	3.8×10^{10}
H/4PTB	−0.62	3.4×10^{11}	MeO/MOB	−0.63	2.9×10^{11}
H/MOB	−0.81	3.8×10^{12}	CF_3/PHB	−0.64	7.9×10^{11}
Me/FPB	−0.14	2.0×10^9	CF_3/4PTB	−0.85	8.4×10^{12}
Me/PHB	−0.31	1.2×10^{10}	CF_3/MOB	−1.04	1.2×10^{13}
Me/1OTB	−0.32	2.1×10^{10}	CF_3/POB	−1.07	1.2×10^{13}
Me/2OTB	−0.36	2.6×10^{10}	NO_2/PHB	−0.72	2.6×10^{12}
Me/1PTB	−0.39	3.0×10^{10}	NO_2/4PTB	−0.93	1.4×10^{13}
Me/2PTB	−0.44	5.6×10^{10}	NO_2/MOB	−1.12	1.2×10^{13}
Me/3PTB	−0.48	1.0×10^{11}	NO_2/POB	−1.15	1.1×10^{13}
Me/DMB	−0.51	3.0×10^{11}	SO_2CF_3/PHB	−0.83	3.4×10^{12}
Me/4PTB	−0.52	1.7×10^{11}	SO_2CF_3/MOB	−1.23	2.3×10^{13}
Me/MOB	−0.71	1.0×10^{12}			

virtually the same throughout the series. In related intramolecular electron transfer reactions, an increase in distance of ca. 6 Å causes k_{et} to decrease by ca. 100 times.[17] On the basis of these experiments, it appears that the impenetrable sphere model for the borate anion is not valid.

Molecular mechanics calculations predict a penetrated ion pair structure for the cyanine borates (see below). We attempted to probe one aspect of this prediction by examination of the bulky *ortho*-substituted borates and tetrakis(3,5-di-*tert*-butylphenyl)borate (DBB). Two of the borates in the *ortho* series of mixed borates, *o*-tolyl groups, 3OTB and 4OTB, are predicted to increase r_{DA} compared with the *para*-substituted borates. The substituents on these borates should keep the cyanine from penetrating so deeply and thereby slow k_{et}. Unfortunately, however, the experimental data, collected in Table 4, are too imprecise to support this conjecture.

We measured k_{et} for the series of 5,5′-substituted cyanines with *para*-substituted tetraarylborates. These substituents do not inhibit penetration. The results of these experiments are summarized in Table 5 and are shown graphically as a Marcus plot in Figure 3. Analysis of these data with classical Marcus theory gives $k_{max} = 2 \times 10^{13}$ s^{-1} and $\lambda = 1.3$ eV.

Bond Rotation in H-Cy TRPB. The concept of a penetrated ion pair structure for the cyanine borate has implications beyond effects on k_{et}. Typically, the most important internal conversion pathway of excited cyanines is rotation about one of the central carbon−carbon bonds.[11-18] If the dye is penetrated into the borate, this rotation should be hindered and the excited state lifetime should increase. We tested this prediction by examination of *tetrakis*(4-triptycenylphenyl)borate (TRPB).[19] The calculated structure of this ion pair structure is shown in Figure 4. The singlet lifetimes of H-Cy (τ_s) with PF_6^-, and tetrakis(4-cyclohexylphenyl)borate (CHPB), examined for comparison, were measured using picosecond absorption and fluorescence spectroscopy in a variety of aromatic hydrocarbon solutions. The data are collected in Table 6. The singlet lifetime of H-Cy with TRPB as the counterion is greater than it is for PF_6^- and CHPB anions in all solvents studied. Since rotational internal conversion normally accounts for ca. 90% of the decay of the excited cyanine, a reduction in $k_{rot.}$ will cause an increase in τ_s.

Intra-Ion Pair Nuclear Overhauser Effect. The structure of the cyanine borate was probed by measuring the intra-ion pair ^1H nuclear Overhauser effect.[20] A solution of H-Cy CHPB in benzene was examined—the structures and the observed signals are shown in Figure 5. The intermolecular signals reveal that only the front side of the dye is in close contact with the borate. Furthermore, the borate holds the cyanine rather tightly since no signals from protons on the cyclohexyl ring are observed. The observed Overhauser effects are only consistent with a penetrated ion pair with a front approach (see Scheme 1 for definitions of front and back orientations). They do not, however, distinguish between symmetrical and asymmetrical structures.

Molecular Mechanics Calculations. The structure adopted by the cyanine borate ion pair is determined by a balance between Coulombic attraction and van der Waals repulsion. Since the Coulombic attraction and molecular size are approximated well by force-field calculations,[21] we used MMX with the PCMODEL program[22] to predict their structure.

The trial structure for calculation was assembled with the cyanine at less than van der Waals contact from the borate so that energy minimization pushed the dye away from the borate. The global minimum was sought by varying the initial orientation of the cyanine and borate. The following configurations for H-Cy and BBPB are shown in Figure 6: side approach, back approach, symmetrical front approach, and asymmetrical front approach. The calculated values for the free energy of formation ($\Delta G_{form.}$), the heat of formation (ΔH_{form})., the Coulombic attraction ($E_{coul.}$), and the boron to the central cyanine carbon distance ($B-C_{cent.}$) are shown in Table 7.

The two frontal approaches have the lowest energies with the asymmetrical approach lower by ~4 kcal/mol. This relatively small energy difference indicates that the cyanine probably swings back and forth in the borate pocket passing through the symmetrical structure. The distance from the boron atom to the central carbon atom in the cyanine changes by only 0.3 Å for the two frontal

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(16) The singlet lifetimes of the cyanine dyes were measured by time-resolved absorption spectroscopy, and k_{et} was estimated from fluorescence yields as previously described.

(17) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

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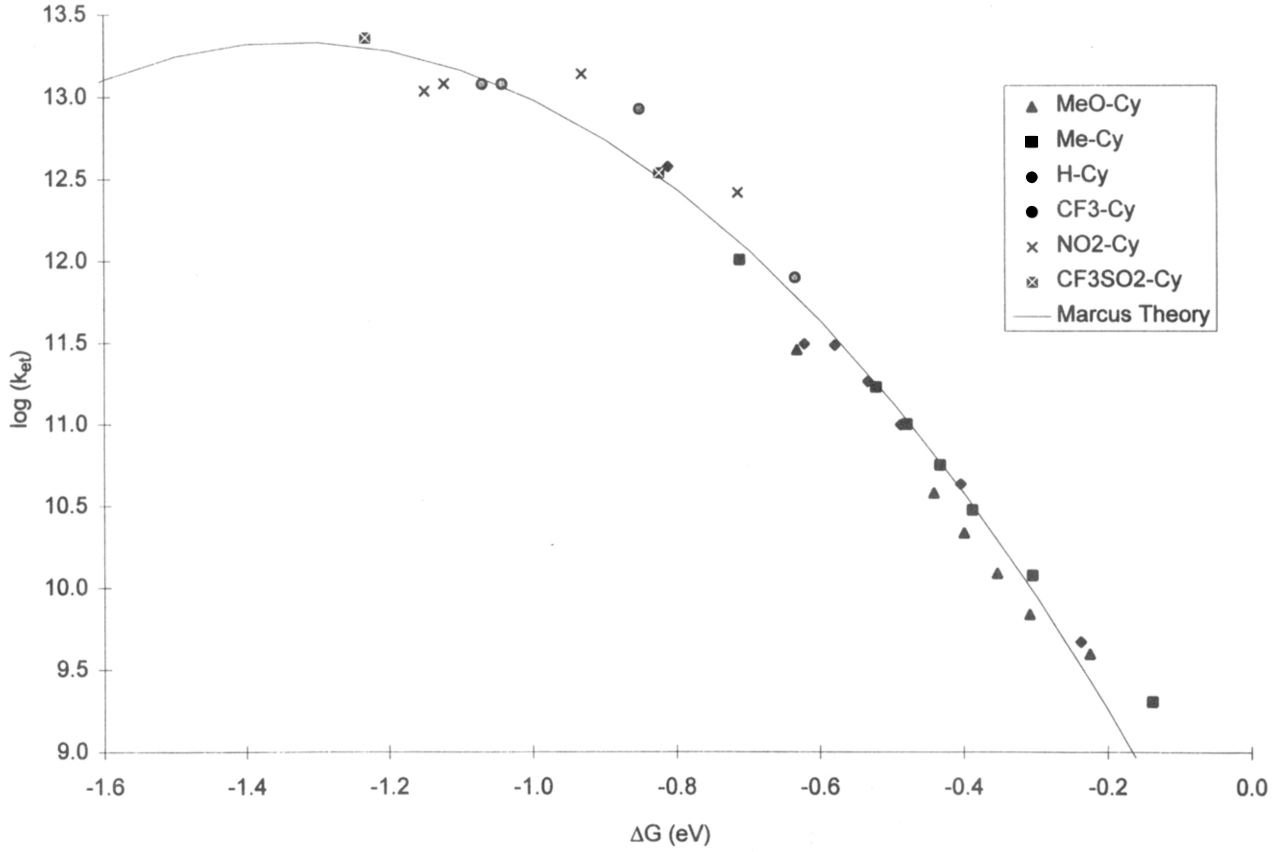

Figure 3. Log of rate constants for intraion pair electron transfer reactions of cyanine borates in benzene solution (the points correspond to the particular cyanine dyes indicated in the box). The solid line is the best fit of these data to classical Marcus theory.

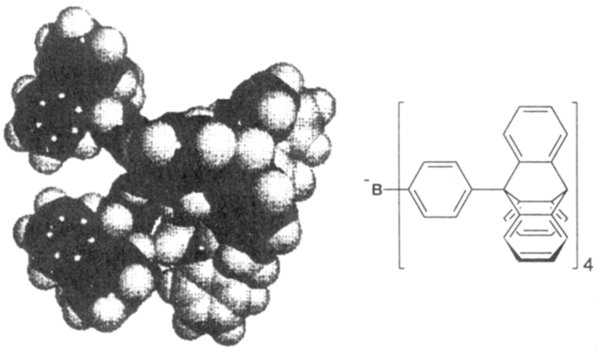

Figure 4. Calculated structure of TRPB with cyanine dye.

Table 6. Lifetimes of H-Cy with Different Counterions

solvent	τ_s (ps), PF_6	τ_s (ps), TRPB	τ_s (ps), CHPB
benzene	250	520	28
toluene	300	490	13
p-xylene	350	400	8
tetralin	435	670	6

approaches. A random dot stereogram of H-Cy BBPB, Figure 7, shows the frontal approach in three dimensions.

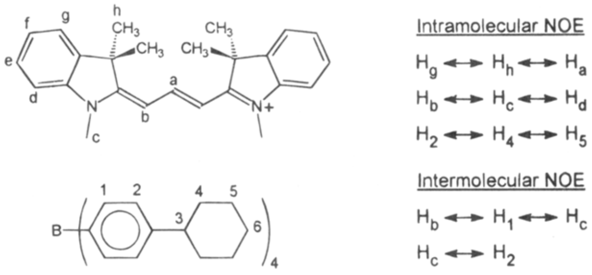

Figure 5. Observed nuclear Overhauser effects for the cyanine borate ion pair.

Discussion

A prime objective of the work described in this paper is to discern the structure and properties of cyanine borate salts dissolved in nonpolar solvents such as benzene. Four strategies designed to accomplish this goal were pursued: (i) analysis of the distance dependence of the electron transfer rate constant, (ii) investigation of effect of variation of borate size on the photophysical properties of the cyanine (iii) measurement of intra-ion pair nuclear Overhauser effects, and (iv) computation of the structure by molecular mechanics methods. Each experiment reveals a different aspect of the cyanine borate structure, but all are consistent with a contact ion pair where the center-to-center distance between the ions is less than the sum of the radii of the individual ions assuming that they are spheres or cylinders. We call such structures penetrated ion pairs.

The crudest view of the structure of the cyanine borate ion pair is revealed by the examination of the structure dependence of k_{et}. Fundamentally, increasing the radius of the borate, which must lead to an increase in r_{DA} if the conventional hard-sphere picture of contact ion pairs is valid, has essentially no effect on k_{et}. This result is consistent with an ion pair structure where the cyanine cation has access to the interior of the borate anion. In particular, the inhibition of k_{et} by TRPB is consistent with this model and supports the view that estimated "center-to-center" distances control the electron transfer rate constant.

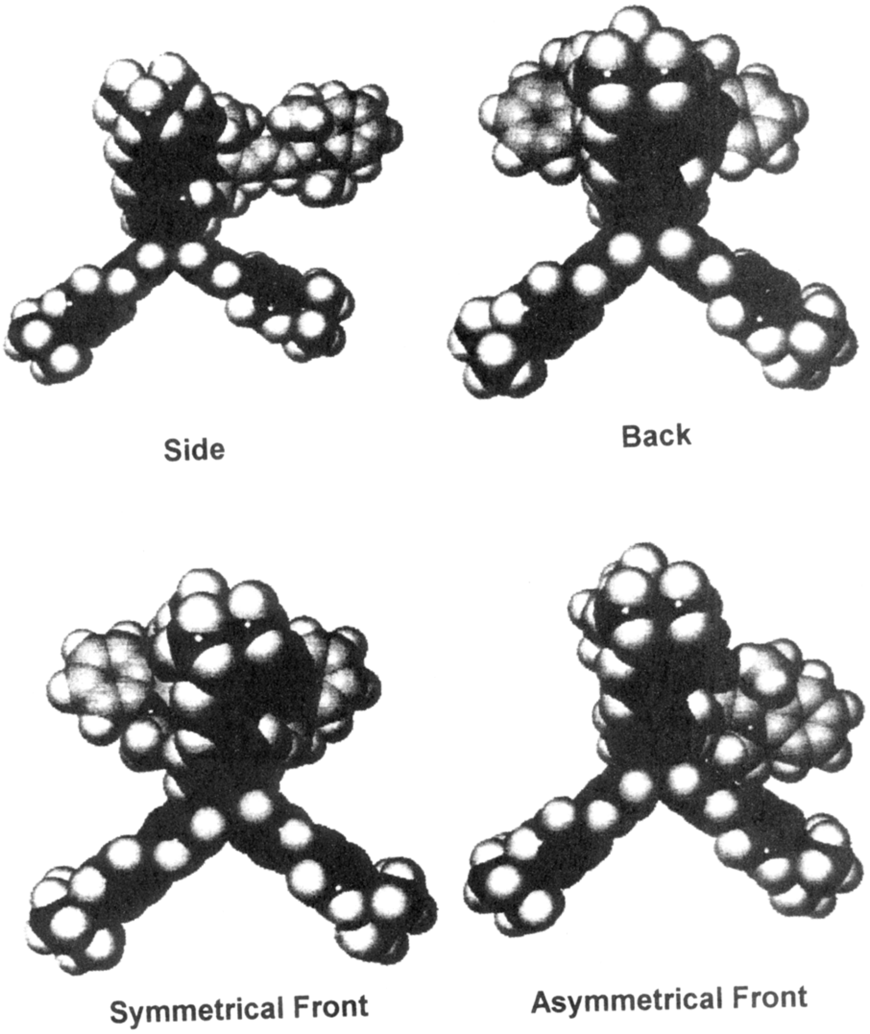

Figure 6. Calculated structures for side, back, symmetrical front, and asymmetrical front penetration of H-Cy in CHPB.

Table 7. Calculated Energies and Distances for Various Approaches of H-Cy BBPB

approach	ΔG_{form} (kcal/mol)	ΔH_{form} (kcal/mol)	E_{coul} (kcal/mol)	B-C_{cent} (Å)
side	115	185	46	8.5
back	114	182	39	6.9
symm front	103	173	51	5.7
asymm front	97	167	54	5.4

A more refined view of the structure of the cyanine borate ion pair is developed by analysis of the properties of the CyTRPB. Unlike the other *p*-alkyl-substituted borates we examined, the triptycenyl groups have three-dimensional bulk which inhibits access by the cyanine to the interior of the borate. If the cyanine penetrates this cavity, its motions must be restricted by contact with the triptycenyl groups. We find, in benzene solution, that the lifetime of singlet excited CyTRPB is longer than it is for the PF_6^- salt . Significantly, the lifetime of CyCHPB is ca. 10 times less than CyTRPB even though the two borates are expected to have essentially the same oxidation potential. These results indicate that the rate constant for rotation of the excited singlet state is reduced by association with the triptycenyl borate. In effect, the triptycenyl groups cause an increase in the viscosity sensed by the cyanine cation. This can only be understood if the cyanine penetrates into the space occupied by the triptycenyl groups of this borate.

Electron transfer to the excited cyanine from the TRPB anion is thermodynamically feasible. If the dye is held back from the electron-donating orbitals of the borate by the triptycenyl groups, k_{et} will be slowed. With the data available it is not possible to distinguish quantitatively between reduction of k_{et} and inhibition of rotation of the excited state of the dye. Consider the experiments conducted in toluene solution. If we assume that electron transfer is completely stopped as one extreme, then the rotational relaxation rate constant[23] is decreased from 2.8×10^9 s^{-1} to 1.5×10^9 s^{-1} by association with the TRPB anion. At another extreme, electron transfer could be occurring, and the rotational relaxation process could be stopped completely. For this case, the electron transfer rate is still 35 times slower than it is for the CHPB anion. Whichever extreme is closer to reality, these results indicate that k_{et} is reduced in the TRPB salt. The most reasonable explanation for this finding is that the cyanine cation is being held at a greater distance in TRPB than it is in CHPB. This is consistent with the proposed penetrated ion pair structure for cyanine borates.

The nuclear Overhauser effects observed for CyCHPB demand a close association of the cyanine and borate, but they do not reveal a precise structure. As seen in Scheme 1, the borate can approach the dye from the front, the back, or either side. The approaches from the top and bottom of the page are ruled out because the aryl groups on the borate will block out such a wide structure. The

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[23] Murphy, S.; Sauerwein, S; Drickamer, H. G.; Schuster, G. B. *J. Phys. Chem.*, in press.

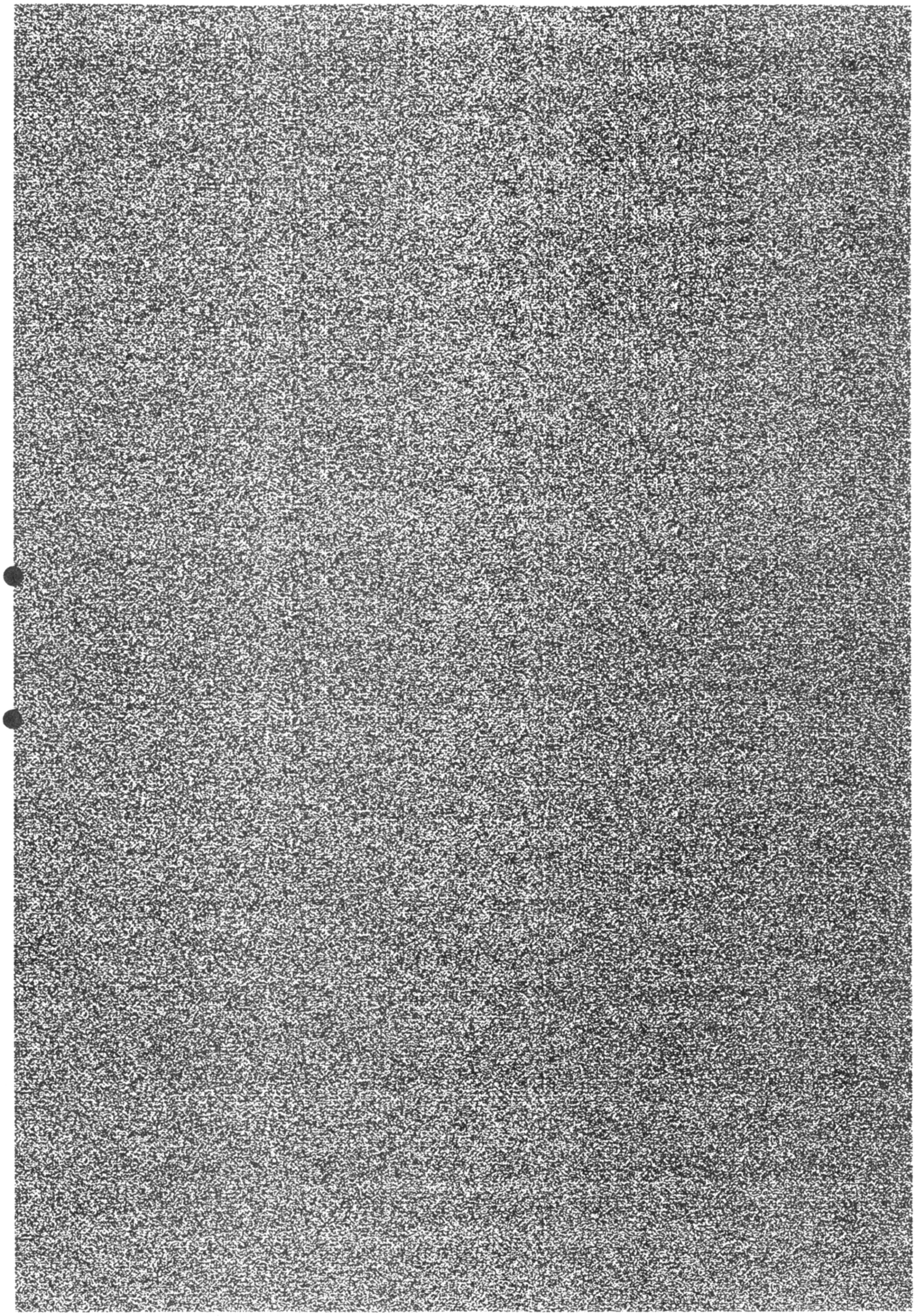

Figure 7. Calculated structure of front-penetrated H-Cy BBPB. To view the stereogram, hold the page at arms length and focus behind the page. It is possible to resolve the individual atoms and see the exact calculated structure of the cyanine borate ion pair.

structures in which the borate approaches from the front, back, and side were calculated using PCMODEL, and the front approach was found to be favored by ca. 15 kcal/mol. These calculations clearly are consistent with the NOE experiments and show that the borate anion does not behave as a hard sphere when it forms an ion pair with the cyanine cation. Instead, in response to a significant reduction in energy due to Coulombic attraction, the dye enters crevices between the aryl groups of the borate and a penetrated ion pair results.

Conclusions

In benzene solution, cyanine borate salts exist as penetrated ion pairs where the cation has entered crevices in the anion. The cyanine penetrates with the *N*-methyl groups pointed toward the boron atom (frontside) and forms a symmetrical structure or a pair of isoenergetic asymmetrical structures. Penetration affects the physical properties of the cyanine dye. In its excited singlet state, both rotation to the *cis*-isomer and electron transfer can be affected by penetration. Formation of penetrated ion pairs should be considered whenever the partners in a contact ion pair are not hard spheres.

Experimental Section

General. Absorption spectra were recorded with a Varian Cary 1E UV−vis spectrophotometer. Fluorescence spectra of cyanine borates in benzene solution were recorded with a Spex Fluorolog F111. Quantum yields for the fluorescence of cyanine borates were determined on freshly prepared solutions by comparison with the fluorescence of cyanine hexafluorophosphate in benzene solution ($\Phi = 0.047$). A Hewlett-Packard 5970 series mass selective detector was used for low-resolution mass spectrometry. High-resolution electron ionization and field ionization mass spectra employed a Finnigan-MAT 731. For fast atom bombardment ionization, a Fisons VG ZAB-SE was used for low-resolution spectra and for high resolution a Fisons VG 70-SE-4F was used. ^{1}H and ^{13}C NMR spectra were taken with a 200 MHz Varian XL200 or a 300 MHz General Electric QE300 instrument as noted. Elemental analyses were performed by the University of Illinois Microanalysis Laboratory. The following solvents were freshly distilled prior to use in reaction: tetrahydrofuran (THF) from sodium benzophenone ketyl, diethyl ether from sodium benzophenone ketyl, and benzene from sodium benzophenone ketyl. Flash chromatography was performed on 230−400 mesh silica gel. Melting points were determined by a Büchi melting point apparatus and are uncorrected. Sodium tetraphenylborate and sodium tetrakis(4-fluorophenyl)borate were purchased from the Aldrich Chemical Co.

1,1′,3,3,3′,3′-Hexamethylindocarbocyanine Iodide. According to the procedure given by Hamer,[24] a solution of 4.0 g (13 mmol) of 1,2,3,3-tetramethylindolinium iodide and 1.8 g (12 mmol) of triethyl orthoformate in 37 mL of acetic anhydride was heated at reflux for 0.5 h. The solvent was removed in vacuo, and the dark solid was recrystallized from ethanol to yield 2.1 g (72%) of the cyanine as purple needles.

2,3,3,5-Tetramethylindolenine. The indole was made by the method of Konschegg[25] from tolylhydrazine and methyl iso propyl ketone: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 1 H), 7.11 (s, 1 H), 7.02 (d, J = 8.1 Hz, 1 H), 2.63 (s, 3 H), 2.36 (s, 3 H), 1.33 (s, 6 H); MS (EI, 70 eV) m/z (relative intensity) 173 (77); HRMS m/z for $C_{12}H_{15}N$ calcd 173.1204, obsd 173.1203.

1,2,3,3,5-Pentamethylindolinium Iodide. A solution of 4.0 g (23 mmol) of 2,3,3,5-tetramethylindole in 3.1 mL (23 mmol) of methyl tosylate was heated at 130 °C for 3 h. The red solid was dissolved in water, and a 10% potassium hydroxide solution was added to form a white precipitate. The aqueous solution was extracted with ether (3 × 100 mL), and to the combined organic layers was added 10 mL of concd hydriodic acid. The solution was cooled in ice water, and the indolinium salt precipitated out. The crude product was recrystallized from ethanol to afford 2.4 g (32%) of 1,2,3,3,5-pentamethylindolinium iodide as slightly gray flakes. Anal. Calcd for $C_{13}H_{18}NI$: C, 49.38; H, 5.74; N, 4.43; I, 40.45. Found: C, 49.49; H, 5.74; N, 4.31; I, 40.11.

1,3,3,5,1′,3′,3′,5′-Octamethylindocarbocyanine Iodide. A solution of 1.0 g (3.2 mmol) of 1,2,3,3,5-pentamethylindolinium iodide and 0.5 mL (3.2 mmol) of triethyl orthoformate in 10 mL of pyridine was heated at reflux for 1 h. The resulting mixture was poured into water and cooled in an ice bath, and the crystals were collected by vacuum filtration. The product was recrystallized from ethanol to afford 0.82 g (53%) of methylcyanine as purple needles: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.36 (t, J = 13.3 Hz, 1 H), 7.29 (d, J = 13.1 Hz, 2 H), 7.19 (d, J = 7.9 Hz, 2 H), 7.14 (s, 2 H), 7.00 (d, J = 7.9 Hz, 2 H), 3.77 (s, 6 H), 2.42 (s, 6 H), 1.68 (s, 12 H). Anal. Calcd for $C_{27}H_{33}N_2I$ (plus $^1/_2$ H_2O): C, 62.19; H, 6.57; N, 5.37; I, 24.33. Found: C, 62.31; H, 6.63; N, 5.38; I, 23.55.

1,3,3,1′,3′,3′-Hexamethyl-5,5′-dimethoxyindocarbocyanine Iodide. 2,3-Dimethyl-5-methoxyindole, from methoxyphenylhydrazine, and 1,2,3,3-tetramethyl-5-methoxyindolinium iodide were prepared by the method of Nagaraja and Sunthankar.[26] A solution of 1.0 g (3.0 mmol) of 1,2,3,3-tetramethyl-5−methoxyindolinium iodide and 1.0 mL (6.0 mmol) of triethyl orthoformate in 10 mL of freshly distilled 3-picoline was heated at reflux for 1.5 h. The solution was poured into water and cooled in ice-water, and the precipitate was collected by vacuum filtration. The purple solid was recrystallized from ethanol acidified with concd hydriodic acid to afford 0.54 g (64%) of the methoxycyanine as purple needles: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.44 (t, J = 13.5 Hz, 1 H), 7.25 (d, J = 8.7 Hz, 2 H), 7.14 (d, J = 2.5 Hz, 2 H), 6.97 (dd, J = 2.5 Hz, 8.7 Hz, 1 H), 6.28 (d, J = 13.6 Hz, 1 H), 3.84 (s, 6H), 3.61 (s, 6 H), 1.73 (s, 12 H). Anal. Calcd for $C_{27}H_{33}N_2I$ (plus $1H_2O$): C, 57.65; H, 6.27; N, 4.98; I, 22.56. Found: C, 57.67; H, 6.28; N, 4.87.

4-Nitrobenzotribromide. *p*-Nitrobenzal bromide was prepared by bromination of *p*-nitrotoluene at 170−180 °C by the method of Jones.[27] *p*-Nitrobenzotribromide was prepared by its reaction with sodium hypobromite solution using the procedure described by Fisher:[28] mp 80−83 °C (lit.[27] mp 86−87 °C). Anal. Calcd for $C_7H_8NO_2Br_3$: C, 22.49; H, 1.08; N, 3.75. Found: C, 22.53; H, 1.09; N, 3.73.

4-Nitrobenzotrifluoride. *p*-Nitrobenzotribromide was heated with antimony trifluoride according to the method of Jones[27] to give *p*-nitrobenzotrifluoride as white flakes: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.37 (d, J = 8.6 Hz, 2 H), 7.85 (d, J = 8.6 Hz, 2 H).

4-Aminobenzotrifluoride. This compound was prepared by the procedure described by Jones:[27] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2 H), 6.69 (d, J = 8.6 Hz, 2 H).

4-(Trifluoromethyl)phenylhydrazine Hydrochloride. To a solution of 10.3 g (64 mmol) of 4-aminobenzotrifluoride in 40 mL of concd hydrochloric acid cooled in an ice−water bath was added dropwise a solution of 5.2 g (75 mmol) of sodium nitrite in 25 mL of water, keeping the reaction temperature below 3 °C. A chilled solution of stannous chloride dihydrate in 38 mL of concd hydrochloric acid (34.8 g, 154 mmol) was then added dropwise to the cooled diazonium salt solution, keeping the reaction below 5 °C. The mixture was stirred an additional hour at 0 °C. The tan solid was collected by vacuum filtration, dissolved in hot water, and filtered, and 9.1 g (67%) of the hydrazine salt precipitated out as slightly yellow needles: ^{1}H NMR (200 MHz, CD_3OD) δ 7.63 (d, J = 8.6 Hz, 2 H), 7.06 (d, J = 8.6 Hz, 2 H).

5-(Trifluoromethyl)-1,2,3,3-tetramethylindolinium Iodide. To a solution of 2.0 g (9.4 mmol) of the trifluoromethylhydrazine hydrochloride and 0.81 g (9.4 mmol) of methyl isopropyl ketone in 5 mL of absolute ethanol cooled in an ice−water bath was added 0.61 g (8.8 mmol) sodium ethoxide. The

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(24) Hamer, F. M. *J. Chem. Soc.* **1927**, 2796−804.

(25) Konschegg, A. *Monat. Chem.* **1905**, *26*, 931.

(26) Nagara, S. N.; Sunthankar, S. V. *Sci. Ind. Res.* **1958**, *17B*, 457.

(27) Jones, R. G. *J. Am. Chem. Soc.* **1947**, *69*, 2346.

(28) Fisher, H. C. *J. Am. Chem. Soc.* **1934**, *56*, 2469.

mixture was heated at reflux for 3.5 h, the solvent was removed in vacuo, and the hydrazone was distilled at 0.35 Torr collecting all of the distillate. A 16 mL portion of 2 N sulfuric acid was added and the solution was heated at reflux for 1.5 h. The solution was cooled, saturated. sodium bicarbonate solution was added until it was neutral, and the indole was extracted with ether (2 × 20 mL). The combined organic layers were dried with magnesium sulfate, filtered, and concentrated in vacuo to give 1.2 g (55%) of the indolenine as a yellow oil. The crude indolenine was methylated by heating with 1.9 g (13 mmol) of iodomethane in 10 mL of anhydrous methanol in a sealed tube at 100−110 °C for 5 h. The solvent was removed in vacuo, and the resulting red solid was dissolved in hot water, filtered, and cooled to yield 0.97 g (51% from indole) of the (trifluoromethyl)indolinium iodide. Indolenine: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (s, 2 H), 7.51 (s, 1 H), 2.32 (s, 3 H), 1.33 (s, 6 H). Indolinium salt: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.90 (s, 2 H), 7.78 (s, 1 H), 4.33 (s, 3 H), 3.16 (s, 3 H), 1.75 (s, 6 H). Anal. Calcd for $C_{13}H_{15}NF_3I$ (+$^1/_2$ H_2O): C, 41.29; H, 4.26; N, 3.70. Found: C, 41.26; H, 4.36; N, 3.67.

1,3,3,1′,3′,3′-Hexamethyl-5,5′-bis(trifluoromethyl)indocarbocyanine Iodide. A solution of 0.51 g (1.4 mmol) of the (trifluoromethyl)indolinium iodide and 0.42 g (2.8 mmol) of triethyl orthoformate in 5 mL of pyridine was heated at reflux for 40 h. The solution was poured into 10 mL of water and cooled in an ice−water bath. The gray powder which formed was collected by vacuum filtration and recrystallized from ethanol acidified with a few drops of concentrated hydriodic acid to produce 0.25 g (58%) of the (trifluoromethyl)cyanine: ^{1}H NMR (300 MHz, CD_3CN) δ 8.50 (t, J = 13.5 Hz, 1 H), 7.84 (s, 2 H), 7.76 (d, J = 8.3 Hz, 2 H), 7.40 (d, J = 8.3 Hz, 2 H), 6.40 (d, J = 13.5 Hz, 2 H), 3.60 (s, 6 H), 1.73 (s, 12 H). Anal. Calcd for $C_{27}H_{27}N_2F_{12}P$ (analyzed as the hexafluorophosphate salt): C, 50.79; H, 4.26; N, 4.39; F, 35.71. Found: C, 50.78; H, 4.24; N, 4.40; F, 35.62.

2,3,3-Trimethyl-5-nitroindolenine. A solution of 5.0 g (29 mmol) of 4-nitrohydrazine stabilized with 10% water (supplied by Aldrich Chemical Co.) and 2.5 g (29 mmol) of methyl isopropyl ketone in 50 mL of absolute ethanol was heated at reflux for 1 h. The solvent was removed in vacuo, and 25 mL of concd hydrochloric acid and 25 mL of glacial acetic acid were added to the black solid. The mixture was heated for 3 h and then cooled to room temperature. The black solution was neutralized with a 10% potassium hydroxide solution during which time a yellow precipitate formed. The mixture was cooled to 0 xbcC and the yellow solid collected by vacuum filtration and recrystallized from ethanol after treating with decolorizing carbon. A second fraction was obtained by extracting the aqueous filtrate with 3 × 100 mL of ether. The organic layers were combined, washed with saturated sodium chloride solution, dried with magnesium sulfate, filtered and concentrated in vacuo. The resulting solid was purified as above. The reaction yielded 1.9 g (31%) of the nitroindolenine as yellow plates: mp 119−121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (dd, J = 8.5 Hz, 2.2 Hz, 1 H), 8.15 (d, J = 2.2 Hz, 1 H), 7.60 (d, J = 8.5 Hz, 1 H), 2.35 (s, 3 H), 1.37 (s, 6 H); MS (EI, 70 eV), m/z (relative intensity) 204 (100). Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.70; H, 5.94; N, 13.72.

1,2,3,3-Tetramethyl-5-nitroindolinium Iodide. A solution of 1.3 g (6.5 mmol) of the nitroindole and 1.9 g (13 mmol) of iodomethane in 5 mL of anhydrous methanol was heated for 6 h at 100−110 °C in a sealed tube. The contents were concentrated in vacuo, dissolved in 70 mL of hot water, and filtered, and the resulting red solution was cooled to produce 1.6 g (73%) of the nitroindolinium salt as fine, yellow needles: mp 210 °C dec; ^{1}H NMR (300 MHz, CD_3CN) δ 8.58 (d, J = 2.1 Hz, 1 H), 8.48 (dd, J = 8.8 Hz, 2.2 Hz, 1 H), 7.92 (d, J = 8.8 Hz, 1 H), 3.98 (s, 3 H), 2.78 (s, 3 H), 1.61 (s, 6 H).

1,3,3,1′,3′,3′-Hexamethyl-5,5′-dinitroindocarbocyanine Hexafluorophosphate. A solution of 0.54 g (1.6 mmol) of nitroindolinium iodide and 0.46 g (3.1 mmol) of triethyl orthoformate in 10 mL of acetic anhydride was heated at reflux for 1 h. The mixture was cooled in ice−water, and the gray precipitate was collected by vacuum filtration. The crude product was dissolved in a minimum amount of hot acetonitrile, and a solution of potassium hexafluorophosphate (0.6 g, 3.3 mmol) in 50 mL of water was added. The solution was hot filtered and cooled, and the crystals which formed were collected by vacuum filtration to give 0.31 g (67%) of the nitrocyanine: ^{1}H NMR (300 MHz, CD_3CN) δ 8.52 (t, J = 13.5 Hz, 1 H), 8.39 (d, J = 2.2 Hz, 2 H), 8.35 (dd, J = 8.7 Hz, 2.2 Hz, 2 H), 7.42 (d, J = 8.7 Hz, 2 H), 6.44 (d, J = 13.5 Hz, 2 H), 3.61 (s, 6 H), 1.76 (s, 12 H). Anal. Calcd for $C_{25}H_{27}N_4O_4PF_6$ (+2CH_3CN): C, 51.63; H, 4.93; N, 12.46. Found: C, 51.47; H, 5.03; N, 12.37.

1,3,3,1′,3′,3′-Hexamethyl-5,5′-dinitroindocarbocyanine *dl*-10-Camphor Sulfonate. A mixture of the nitrocyanine chloride (60 mg, 0.12 mmol)[29] and 400 mg (7.1 mmol) of potassium hydroxide in 30 mL acetonitrile and 40 mL water was heated until it dissolved. The solution was cooled, and a stream of nitrogen was blown over the solution to precipitate 32 mg (55%) of the hydroxide−cyanine adduct as a red solid. This adduct was dissolved in 18 mL of hot methanol, and *dl*-10-camphorsulfonic acid (174 mg, 0.75 mmol) in 2 mL of water was added followed by five drops of 10% potassium hydroxide solution; the solution was cooled, and evaporation under a stream of nitrogen caused precipitation of 38 mg (81% from alcohol) of cyanine sulfonate. Hydroxide−cyanine adduct: ^{1}H NMR (300 MHz, CD_3CN) δ 8.10 (m, 2 H), 7.99 (d, J = 2.4 Hz, 1 H), 7.88 (d, J = 2.4 Hz, 1 H), 6.98 (dd, J = 11.8 Hz, 15.1 Hz, 1 H), 6.70 (d, J = 8.8 Hz, 1 H), 6.52 (d, J = 8.7 Hz, 1 H), 5.64 (d, J = 11.8 Hz, 1 H), 5.58 (d, J = 15.1 Hz, 1 H), 3.88 (s, 1 H), 3.15 (s, 3 H), 2.81 (s, 3 H), 1.58 (s, 3 H), 1.56 (s, 3 H), 1.29 (s, 3 H), 1.06 (s, 3 H).

1,2,3,3-Tetramethyl-5-fluorolinium Iodide. A solution of 1.5 g (9.2 mmol) of the fluoroindole[30] and 1.26 mL (20 mmol) of iodomethane in 3 mL of anhydrous methanol was heated for 24 h at 100−110 °C in a sealed tube. The contents of the tube were concentrated in vacuo, dissolved in of hot water, and filtered, and the resulting mixture was cooled to produce the fluoroindolinium iodide (52% yield): mp 230 °C dec; ^{1}H NMR (300 MHz, MeOD) δ 7.0 - 8.4 (m, 3 H), 4.10 (s, 3 H), 2.20 (s, 3 H), 1.80 (s, 3 H).

1,3,3,1′,3′,3′-Hexamethyl-5,5′-difluorodocarbocyanine Iodide. A solution of 0.80 g (2.5 mmol) of the fluorindolinium iodide and 0.42 g (2.5 mmol) of triethyl orthoformate in 20 mL of acetic anhydride was heated at reflux for 32 h. The mixture was cooled in ice−water and the precipitate was collected by vacuum filtration to give 49% of the fluorocyanine.

4-(Trifluoromethyl)thio)phenylhydrazine Hydrochloride. To an ice−water-cooled slurry of 6.8 g (35 mmol) of 4-(trifluoromethyl)mercaptoaniline[31] in 40 mL of concd hydorchloric acid was added dropwise a chilled solution of 3.0 g (42 mmol) of sodium nitrite in 20 mL of water, keeping the temperature below 2 °C. The solution was stirred for an additional hour at 0 °C, and then a chilled solution of 19 g (84 mmol) of stannous chloride dihydrate in 25 mL of concd hydrochloric acid was added dropwise, keeping the temperature below 2 °C. The mixture was stirred for an 1 h in an ice−water bath, and the resulting tan foam was collected by vacuum filtration and washed with hexane. The tan solid was dissolved in hot water containing a few drops hydrochloric acid, hot filtered, and then cooled to yield 4.3 g (50%) of the hydrazine hydrochloride: ^{1}H NMR (300 MHz, CD_3OD) δ 7.64 (d, J = 8.9 Hz, 2 H), 7.02 (d, J = 8.7 Hz, 2 H); MS (EI, 70 eV) m/z (relative intensity) 208 (86). Anal. Calcd for $C_7H_8N_2F_3SCl$: C, 34.36; H, 3.30; N, 11.45; F, 23.30; S, 13.10; Cl, 14.49. Found: C, 34.08; H, 3.43; N, 11.16; F, 23.08; S, 13.06; Cl, 14.41.

5-((Trifluoromethyl)thio)-1,2,3,3-tetramethylindolinium Iodide. To a solution of 3.0 g (12 mmol) of the (trifluoromethyl)thio hydrazine hydrochloride and 1.0 g (12 mmol) of methyl isopropyl ketone in 10 mL of absolute ethanol was added 0.81 g (12 mmol) of sodium ethoxide. The mixture was heated at reflux for 1 h, and then the solvent was removed in vacuo. The hydrazone was distilled at 0.35 Torr, and all of the liquid was collected. To the resulting liquid was added

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(29) The cyanine chloride was made from the indolinium chloride. The indolinium chloride was formed by recrystallizing the indolinium iodide from water with 100 equiv of sodium chloride. Which halide counterion is used for this experiment is not important.

(30) Quadbeck G.; Rohm E. *Chem Ber.* **1954**, *87*, 229.

(31) Yagupolsky, L. M.; Marenets, M. S. *J. Gen. Chem. USSR (Engl. Trans.)* **1954**, *24*, 885.

16 mL of 2 N sulfuric acid, and the mixture was heated at reflux for 45 min. The solution was diluted with 30 mL of water and neutralized to pH 5 with saturated sodium bicarbonate solution. The organic layers were extracted with 3 × 50 mL ether, combined, washed with 50 mL of saturated sodium chloride solution, dried with magnesium sulfate, filtered, and concentrated in vacuo to give 1.9 g (60%) of the indolenine as a yellow crystalline solid. A solution of 1.9 g (7.4 mmol) of indolenine and 2.3 g (16 mmol) of iodomethane in 10 mL of anhydrous methanol was heated in a sealed tube at 100–110 °C for 6 h. The contents were concentrated in vacuo and then mostly dissolved in hot water. The solution was hot filtered, and the filtrate was cooled in ice–water to yield 1.7 g (57%) of the indolinium iodide. Indolenine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 1 H), 7.54 (d, J = 8.1 Hz, 1 H), 7.53 (s, 1 H), 2.30 (s, 3 H), 1.31 (s, 6 H); MS (EI, 70 eV) *m/z* (relative intensity) 259 (100). Indolinium iodide: ^{1}H NMR (300 MHz, CD_3CN) δ 8.05 (s, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 3.92 (s, 3 H), 2.72 (s, 3 H), 1.56 (s, 6 H); MS (EI, 70 eV) *m/z* (relative intensity) ($M^{\bullet+}$ − HI) 273 (52). Anal. Calcd for $C_{13}H_{15}NF_3SI$: C, 38.92; H, 3.77; N, 3.49; F, 14.21; S, 7.99. Found: C, 38.95; H, 3.77; N, 3.52; F, 14.01; S, 7.92.

5-((Trifluoromethyl)sulfonyl-1,2,3,3-tetramethylindolinium Chloride. A solution of 5-((trifluoromethyl)thio)-1,2,3,3-tetramethylindolinium iodide (0.61 g, 1.5 mmol) and 0.91 g (9.1 mmol) of chromium trioxide was dissolved in 25 mL of concd sulfuric acid and stirred for 75 min. The solution was poured into 100 mL of ice-cooled water. The neutral 5-((trifluoromethyl)sulfonyl)-2-methylene-1,3,3-trimethylidolenine was extracted into 100 mL of methylene chloride by continuous extraction. The organic solution was replaced every 10 h with fresh methylene chloride, and three fractions were collected. The organic solution was concentrated in vacuo, and the oil was mostly dissolved in 1.5 M hydrochloric acid and hot filtered to produce the indolinium chloride. The water was removed in vacuo as an azeotrope with ethanol to yield 345 mg (66%) of the indolinium chloride as a yellow solid. Indolenine: ^{1}H NMR (300 MHz, CD_3CN) δ 7.80 (d, J = 8.5 Hz, 1 H), 7.64 (s, 1 H), 6.82 (d, J = 8.5 Hz, 1 H), 4.21 (d, J = 2.2 Hz, 1 H), 4.16 (d, J = 2.2 Hz, 1 H), 3.11 (s, 3 H), 1.33 (s, 6 H); MS (EI, 70 eV), *m/z* (relative intensity) 305 (50). Indolinium chloride: ^{1}H NMR (300 MHz, CD_3CN) δ 8.44 (s, 1 H), 8.34 (d, J = 8 Hz, 1 H), 8.06 (d, J = 8 Hz, 1 H), 3.97 (s, 3 H), 1.61 (s, 6 H); MS (EI, 70 eV) *m/z* (relative intensity) ($M^{\bullet+}$ − HI) 305 (50).

1,3,3,1′,3′,3′-Hexamethyl-5,5′-bis(trifluoromethyl)sulfonyl)indocarbocyanine Chloride. A solution of 280 mg (0.82 mmol) of the (trifluoromethyl)thio indolinium chloride and 240 mg (1.6 mmol) of triethyl orthoformate in 5 mL of acetic anhydride was stirred at room temperature for 5 h. The solvent was removed at ca. 1 Torr at room temperature. The resulting purple solid was recrystallized from ethanol/water acidified with a few drops of hydrochloric acid to produce 63.5 mg (24%) of the sulfone–cyanine: ^{1}H NMR (300 MHz, CD_3CN) δ 8.55 (t, J = 13.5 Hz, 1 H), 8.19 (s, 2 H), 8.16 (d, J = 8.5 Hz, 2 H), 7.58 (d, J = 8.5 Hz, 2 H), 6.56 (d, J = 13.5 Hz, 2 H), 3.64 (s, 6 H), 1.76 (s, 12 H); MS (FAB) *m/z* (relative intensity) (M^+) 621 (100). Anal. Calcd for $C_{27}H_{27}N_2S_2O_4F_{12}P$ (analyzed as the hexafluorophosphate salt): C, 42.30; H, 3.55; N, 3.65. Found: C, 42.17; H, 3.68; N, 3.63.

Cyanine Hexafluorophosphate Salts (General Procedure). The cyanine halide salts were dissolved in a minimum amount of hot acetonitrile, and 1–5 equiv of potassium hexafluorophosphate in water was added. More water was then added until a precipitate which formed dissolved slowly (a few seconds). The solution was allowed to cool in the dark, and the resulting metallic-looking crystals were collected by vacuum filtration and dried under vacuum overnight.

General Procedure for Synthesis of Tetraarylborate Salts. The synthesis is based on the method reported by Vandenberg et al.[32] The tetraarylborates were prepared from the corresponding arylmagnesium bromide and sodium tetrafluoroborate. The aryl bromide was converted to the arylmagnesium bromide using approximately 1 equiv of magnesium turnings by heating a THF or ether solution at reflux. To this solution was added 0.95 equiv of sodium tetrafluoroborate, and the mixture was heated at reflux overnight. The reaction mixture was concentrated in vacuo, and the residue was dissolved in acetonitrile and water. (Approximately 40 mL of acetonitrile and 10 mL of water per gram of starting bromide was used.) This solution was extracted once with a half equal volume of hexane, and the aqueous portion was filtered to remove any undissolved salts. To the aqueous solution was added 5–10 equiv of tetramethylammonium chloride to exchange cations with the borate. The solution volume was reduced by passing a stream of nitrogen over the solution to evaporate the acetonitrile and precipitate the tetramethylammonium borate. The borate was collected by vacuum filtration, dried under vacuum, and recrystallized from acetonitrile/water if necessary.

4-Bromo-4′-methylbiphenyl. According to the procedure of Gomberg and Pernert,[33] 0.35 mL (6.6 mmol) of bromine was added to a mixture of 1.0 g (5.9 mmol) of 4-methylbiphenyl and 20 mg (0.4 mmol) of iron in 25 mL of carbon tetrachloride under an atmosphere of nitrogen at 0 °C. The mixture was stirred in the dark for 13.5 h at 0 °C. The reaction mixture was diluted with ether (50 mL), washed with saturated sodium bicarbonate solution (2 × 100 mL), water (100 mL), and brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting white solid was recrystallized from methanol to afford 1.0 g (70%) of 4-bromo-4′-methylbiphenyl: mp 129–131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8 Hz, 2 H), 7.44 (d, J = 7 Hz, 2 H), 7.42 (d, J = 8 Hz, 2 H), 7.24 (d, J = 7 Hz), 2.39 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) 140.04, 137.47, 137.08, 131.78, 129.59, 128.51, 126.74, 121.14, 21.09; MS (EI, 70eV) *m/z* (relative intensity) 246 (96), 248 (100); HRMS *m/z* for $C_{13}H_{11}Br$ calcd 246.0044, obsd 246.0045. Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.49; Br, 32.33. Found: C, 62.99; H, 4.52; Br, 32.54.

Tetramethylammonium tetrakis(4′-methyl-4-biphenylyl)borate: ^{1}H NMR (200 MHz, CD_3CN) δ 7.49 (d, J = 8.3 Hz, 8 H), 7.43–7.40 (m, 8 H), 7.33 (d, J = 7.1 Hz, 8 H), 7.20 (d, J = 8.3 Hz, 8 H), 3.02 (s, 12 H), 2.33 (s, 12 H). Anal. Calcd for $C_{56}H_{56}NB$: C, 89.22; H, 7.49; N, 1.86; B, 1.43. Found: C, 89.21; H, 7.54; N, 1.62; B, 1.42.

Bromo-4′-*tert*-butylbiphenyl. To a solution of 1.0 g (4.3 mmol) of 4-bromobiphenyl and 0.5 mL (4.7 mmol) of *tert*-butyl chloride in 10 mL of carbon tetrachloride was added 50 mg (0.4 mmol) of aluminum trichloride under an atmosphere of nitrogen at 0 °C. The mixture was stirred at 0 °C for 45 min. The reaction mixture was washed with saturated sodium bicarbonate solution (2 × 50 mL), water (50 mL), and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting white solid was recrystallized from methanol to afford 0.9 g (74%) of 4-bromo-4′-*tert*-butylbiphenyl: mp 137–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8 Hz, 2 H), 7.48 (d, J = 3 Hz, 4 H), 7.45 (d, J = 8 Hz), 1.36 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) 150.69, 139.89, 137.01, 131.76, 128.54, 126.54, 125.82, 121.16, 34.54, 31.30; MS (EI, 70 eV) *m/z* (relative intensity) 288 (34), 290 (33); HRMS *m/z* for $C_{16}H_{17}Br$ calcd 288.0514, obsd 288.0514. Anal. Calcd for $C_{16}H_{17}Br$: C, 66.45; H, 5.92; Br, 27.63. Found: C, 66.47; H, 5.91; Br, 27.51.

Tetramethylammonium tetrakis(4′-*tert*-butyl-4-biphenylyl)borate: ^{1}H NMR (200 MHz, CD_3CN) δ 7.56–7.32 (m, 32 H), 3.04 (s, 1 H), 1.32 (s, 36 H). Anal. Calcd for $C_{68}H_{80}NB$: C, 88.56; H, 8.74; N, 1.52; B, 1.17. Found: C, 88.59; H, 8.72; N, 1.50; B, 1.12.

Tetra-*n*-butylammonium Tetrakis(4-biphenylyl)borate. To a solution of 2.0 g (8.6 mmol) of 4-bromobiphenyl in 200 mL of ether at 0 °C was added 5.4 mL of 1.6 M *n*-butyllithium solution in hexanes. The solution was stirred for 3 h at 0 °C, and then 0.21 mL (1.7 mmol) of freshly distilled boron trifluoride etherate was added. The mixture was allowed to warm to room temperature slowly and then stirred overnight. Finally, the mixture was heated at reflux for 1 h. The reaction was quenched with methanol, and the solvent

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was removed in vacuo. The resulting white solid was mostly dissolved in ca. 100 mL of acetonitrile/water, and the organic soluble components were extracted with 100 mL of hexane. The acetonitrile/water layer was filtered, and 2.7 g (8.4 mmol) of tetra-*n*-butylammonium chloride in 20 mL of water was added to the filtrate. A stream of nitrogen was blown over the solution to precipitate 0.86 g (62%) of borate. The salt was recrystallized first from acetonitrile and then from acetonitrile/toluene with a stream of nitrogen blown over the solution to slowly evaporate the acetonitrile: ^{1}H NMR (300 MHz, CD_3CN) δ 7.62 (d, J = 8 Hz, 8 H), 7.46 (m, 8 H), 7.38 (m, 16 H), 7.24 (t, J = 7 Hz, 4 H), 3.04 (m, 8 H), 1.58 (m, 8 H), 1.34 (m, 8 H), 0.96 (t, J = 7 Hz, 12 H). Anal. Calcd for $C_{64}H_{72}NB$: C, 88.76; H, 8.38; N, 1.62. Found: C, 88.74; H, 8.37; N, 1.61.

Tetramethylammonium tetrakis(2-methylphenyl)borate: ^{1}H NMR (200 MHz, CD_3CN) δ 7.30−7.20 (m, 4 H), 6.84−6.69 (m, 12 H), 3.05 (s, 12 H), 1.52 (s, 12 H). Anal. Calcd for $C_{32}H_{40}NB$: C, 85.51; H, 8.97; N, 3.12; B, 2.41. Found: C, 85.37; H, 8.94; N, 3.27; B, 2.44.

Tetramethylammonium tetrakis(4-methylphenyl)borate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.10 (m, 8 H), 6.78 (d, J = 7.6 Hz, 8 H), 3.04 (s, 12 H), 2.18 (s, 12 H). Anal. Calcd for $C_{32}H_{40}NB$: C, 85.51; H, 8.97; N, 3.12; B, 2.41. Found: C, 85.39; H, 9.02; N, 3.20; B, 2.38.

3,5-Di-*tert*-butylbromobenzene. Following the procedure of Bartlett and co-workers,[34] 6.5 mL (120 mmol) of bromine was added to a mixture of 20.0 g (81.2 mmol) of 1,3,5-tri-*tert*-butylbenzene and 0.4 g (7.5 mmol) of iron in 40 mL of carbon tetrachloride under an atmosphere of nitrogen at 0 °C. The mixture was stirred in the dark for 3.5 h at 0 °C. The reaction mixture was diluted with ether (50 mL), washed with 15% potassium hydroxide solution (2 × 100 mL), water (100 mL), and brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting yellow oil was distilled, yielding a clear liquid (bp 50−84 °C (1.0 mm)) which solidified upon cooling. The solid was recrystallized from hexane to afford 5.8 g (26%) of 3,5-di-*tert*-butylbromobenzene: mp 63−65 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33 (s, 3 H), 1.30 (s, 18 H); ^{13}C NMR (50 MHz, $CDCl_3$) 152.95, 125.73, 122.18, 121.05, 34.98, 31.28; MS (EI, 70eV) m/z (relative intensity) 268 (13), 270 (13). Anal. Calcd for $C_{14}H_{21}Br$: C, 62.46; H, 7.86; Br, 29.68. Found: C, 62.43; H, 7.87; Br, 29.73.

Tetramethylammonium Tetrakis(3,5-di-*tert*-butylphenyl)borate. A mixture of 1.0 g (3.7 mmol) of 3,5-di-*tert*-butylbromobenzene and 0.2 g (28.8 mmol) of lithium wire in 20 mL of ether was heated at reflux for 15 h. The solution was transferred via cannula to another flask and cooled to −78 °C. To this solution was added 0.5 mL of a 1.0 M solution of boron trichloride in hexanes (0.5 mmol), and the solution was stirred at −78 °C for 7 h. The reaction mixture was warmed to room temperature, stirred overnight, and workedup as described above: ^{1}H NMR (200 MHz, CD_3CN) δ 7.42−7.38 (m, 8 H), 6.84 (s, 4 H), 3.05 (s, 12 H), 1.18 (s, 72 H). Anal. Calcd for $C_{60}H_{96}NB$: C, 85.56; H, 11.49; N, 1.66; B, 1.28. Found: C, 85.37; H, 11.55; N, 1.66; B, 1.28.

Tetramethylammonium tetrakis(3,5-dimethylphenyl)borate: ^{1}H NMR (200 MHz, CD_3CN) δ 6.88 (s, 8 H), 6.47 (s, 4 H), 3.02 (s, 12 H), 2.11 (s, 24 H). Anal. Calcd for $C_{36}H_{48}NB$: C, 85.52; H, 9.57; N, 2.77; B, 2.14. Found: C, 85.53; H, 9.68; N, 2.93; B, 2.15.

Tetramethylammonium Tetrakis(4-methoxyphenyl)borate. The borate salt was recrystallized from ethanol: ^{1}H NMR (300 MHz, CD_3CN) δ 7.09 (m, 8 H), 6.59 (d, J = 8.6 Hz, 8 H), 3.68 (s, 12 H), 3.03 (s, 12 H). Anal. Calcd for $C_{32}H_{40}O_4NB$: C, 74.85; H, 7.85; N, 2.73. Found: C, 74.73; H, 7.80; N, 2.72.

4-Bromoisopropoxybenzene. Prepared according to the procedure of Bradley and Robinson[35] by heating isopropyl iodide with 4-bromophenoxide formed from 4-bromophenol and 2-propoxide in isopropyl alcohol. From 40.2 g (0.232 mol) of phenol was obtained 35.0 g (71%) of 4-bromoisoropoxybenzene as a clear liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 8.8 Hz, 2 H), 6.76 (d, J = 8.8 Hz, 2 H), 4.49 (septet, J = 6.1 Hz, 1 H), 1.32 (d, J =6.1 Hz, 6 H); MS (EI, 70eV) m/z (relative intensity) 214 (15), 216 (15).

Tetramethylammonium tetrakis(4-isopropoxyphenyl)borate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.06 (m, 8 H), 6.56 (d, J = 8.4 Hz, 8 H), 4.43 (septet, J = 6.0 Hz, 4 H), 3.03 (s, 12 H), 1.22 (d, J = 6.0 Hz, 24 H); HRMS (FAB) m/z for $C_{44}H_{68}O_4N_2B$ (borate with two ammonium cations) calcd 699.5272, obsd 699.5288. Anal. Calcd for $C_{40}H_{56}O_4NB$ ($+^1/_4$ H_2O): C, 76.24; H, 9.04; N, 2.22. Found: C, 76.19; H, 9.00; N, 2.25.

Triphenyltolylborate Salts. To an ether solution of tolylmagnesium bromide was added 0.5 equiv of dichlorophenylboron, and the solution was heated at reflux overnight. The borate was then treated by the usual procedure described above.

Tetramethylammonium tri(4-methylphenyl)phenylborate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.30−7.20 (m, 3 H), 7.10−7.02 (m, 2 H), 6.93 (dd, J = 7 Hz for both, 2 H), 6.90−6.72 (m, 10 H), 3.05 (s, 12 H), 1.57 (s, 9 H). Anal. Calcd for $C_{31}H_{38}NB$: C, 85.51; H, 8.80; N, 3.22; B, 2.48. Found: C, 85.51; H, 8.80; N, 3.29; B, 2.45.

Tetramethylammonium tri(2-methylphenyl)phenylborate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.26−7.20 (m, 2 H), 7.16−7.06 (m, 6 H), 6.95 (dd, J = 7 Hz for both, 2 H), 6.84−6.76 (m, 7 H), 3.03 (s, 12 H), 2.18 (s, 9 H). Anal. Calcd for $C_{31}H_{38}NB$: C, 85.51; H, 8.80; N, 3.22; B, 2.48. Found: C, 85.43; H, 8.80; N, 3.27; B, 2.43

Diphenylditolylborate Salts. Diphenyl(diethylamino)boron was prepared by the method of Niedenzu and Dawson[36] from 22 g (0.19 mol) of boron trichloride and 14 g (0.19 mol) of diethylamine to form 29.2 g (48%) of dichloro(diethylamino)boron. To 14 g (0.091 mol) of dichloroborane was added phenylmagnesium bromide formed *in situ* and heated at reflux in ether to form 14.1 g (65%) diphenyl(diethylamino)boron. A solution of 14.1 g (0.059 mol) of aminodiphenylborane in 150 mL of hexane was converted to diphenylchloroborane[37] by stirring at −78 °C with 2.1 equiv of boron trichloride for 15 min. The solution was warmed to room temperature and stirred for 5 h. Finally, the solution was heated at reflux for 17 h, concentrated in vacuo, and distilled to afford 11 g (92%) of diphenylchloroborane: bp 90−93 °C (0.4 Torr). The diphenylditolylborate was prepared by addition of tolylmagnesium bromide to the diphenylborane. The borate was then treated by the usual procedure described above.

Tetramethylammonium di(2-methylphenyl)diphenylborate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.24−7.10 (m, 6 H), 6.95 (dd, J = 7 Hz for both, 4 H), 6.88−6.74 (m, 8 H), 3.02 (s, 12 H), 1.66 (s, 6 H). Anal. Calcd for $C_{30}H_{36}NB$: C, 85.50; H, 8.61; N, 3.32; B, 2.57. Found: C, 85.53; H, 8.63; N, 3.35; B, 2.65.

Tetramethylammonium di(4-methylphenyl)diphenylborate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.30−7.20 (m, 4 H), 7.18−7.08 (m, 4 H), 6.96 (dd, J = 7 Hz for both, 4 H), 6.88−6.76 (m, 6 H), 3.05 (s, 12 H), 2.18 (s, 6 H). Anal. Calcd for $C_{30}H_{36}NB$: C, 85.50; H, 8.61; N, 3.32; B, 2.57. Found: C, 85.50; H, 8.64; N, 3.37; B, 2.48.

Triphenyltolylborate Salts. A 0.15 M solution of tolyllithium was made by stirring tolyl bromide and 0.95 equiv of 1.6 M *n*-butyllithium in ether at 0 °C for 3.5 h. The solution was cooled to −78 °C, and 0.65 equiv of a 0.1 M solution of triphenylboron in 3:1 ether:benzene was added. The solution was warmed to room temperature and stirred overnight. The borate was then treated by the usual procedure described above.

Tetramethylammonium (2-methylphenyl)triphenylborate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.26−7.14 (m, 6 H), 7.12−7.04 (m, 1 H), 6.97 (dd, J = 7 Hz for both, 6 H), 6.88−6.74 (m, 6 H), 3.04 (s, 12 H), 1.70 (s, 3 H). Anal. Calcd for $C_{29}H_{34}NB$: C, 85.50; H, 8.41; N, 3.44; B, 2.65. Found: C, 85.51; H, 8.42; N, 3.43; B, 2.78.

Tetramethylammonium (4-methylphenyl)triphenylborate: ^{1}H NMR (300 MHz, CD_3CN) δ 7.34−7.22 (m, 6 H), 7.20−7.10 (m, 2 H), 6.97 (dd, J = 7 Hz for both, 6 H), 6.84−6.80 (m, 5 H), 3.05 (s, 12 H), 2.19 (s, 3 H). Anal. Calcd for

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Table 8. Elemental Analyses for X-Cy Borates

X/borate	calcd			found		
	C	H	N	C	H	N
H/MBPB[a,b]	88.78	7.11	2.69	88.72	7.05	2.60
H/BBPB[c]	88.67	8.11	2.32	88.56	8.32	1.97
H/DMB[d]	85.11	8.31	4.28	85.03	8.25	4.48
H/DBB	86.43	10.12	2.49	86.45	10.15	2.51
H/FLB[b]	78.14	6.09	3.72	78.20	6.00	3.73
H/3PTB[e]	85.50	7.71	4.99	85.60	7.85	5.16
H/2PTB	86.91	7.58	3.97	86.91	7.60	3.99
H/1PTB[d]	85.04	7.49	4.86	85.06	7.58	5.03
H/4OTB[f]	86.86	7.84	3.82	87.02	7.82	3.83
H/3OTB	86.69	7.71	3.90	86.71	7.72	3.87
H/2OTB[g]	85.96	7.60	4.38	86.07	7.70	4.21
H/1OTB	86.94	7.44	4.06	86.95	7.43	4.04
Me/PHB	86.91	7.58	3.97	86.82	7.59	4.00
Me/DMB[h]	85.48	8.55	3.38	85.41	8.51	3.61
Me/DBB[i]	84.43	10.24	2.43	84.26	10.03	2.52
Me/FLB	78.86	6.63	3.61	78.68	6.32	3.42
Me/MOB	80.08	7.45	3.40	79.97	7.40	3.53
Me/4PTB	86.82	8.08	3.68	87.08	8.10	3.76
Me/3PTB[j]	86.33	7.95	4.30	86.23	8.01	4.27
Me/2PTB[k]	85.89	7.84	4.91	85.94	7.86	4.91
Me/1PTB[l]	86.10	7.70	4.74	86.00	7.64	4.70
Me/4OTB	86.82	8.08	3.68	87.07	8.12	3.65
Me/3OTB	86.84	7.96	3.75	86.56	7.89	3.76
Me/2OTB[b]	86.33	7.86	3.80	86.34	7.79	3.84
Me/1OTB	86.89	7.71	3.90	86.88	7.74	3.88
MeO/PHB[d]	81.50	7.30	4.57	81.35	7.21	4.51
MeO/BPB	86.36	6.76	2.72	86.38	6.76	2.70
MeO/DMB[l]	82.88	8.17	4.03	82.51	8.25	4.07
MeO/DBB	84.08	9.95	2.36	83.82	10.12	2.50
MeO/MOB	77.09	7.17	3.27	77.14	7.23	3.51
MeO/4PTB[m]	81.18	7.82	3.84	81.02	7.55	3.63
MeO/3PTB[n]	82.03	7.62	5.12	82.12	7.76	4.97
MeO/2PTB[n]	81.97	7.50	5.21	82.04	7.58	4.96
MeO/1PTB[k]	82.32	7.38	4.80	82.07	7.47	4.77
MeO/4OTB	83.31	7.75	3.53	83.34	7.70	3.74
MeO/3OTB	83.27	7.64	3.60	83.34	7.67	3.61
MeO/2OTB[h]	82.42	7.53	4.04	82.60	7.60	3.91
MeO/1OTB	83.18	7.38	3.73	86.16	7.39	3.72
CF_3/PHB[n]	74.56	5.90	4.92	74.53	5.82	4.66
CF_3 /MOB	70.82	5.94	3.00	70.55	5.88	2.92
CF_3/POB[n]	71.88	6.87	3.87	72.02	6.88	3.71
CF_3/4PTB	76.03	6.38	3.22	75.79	6.35	3.21
NO_2/PHB[d]	75.42	6.27	7.92	75.60	6.18	8.22
NO_2/MOB[b]	71.42	6.28	6.29	71.35	6.18	6.15
NO_2/POB[d]	72.40	7.20	6.13	72.58	7.15	6.12
NO_2/4PTB[o]	76.11	6.81	6.70	76.05	6.76	6.73
SO_2CF_3/PHB[o]	64.90	5.11	3.96	64.76	5.15	3.98
SO_2CF_3/MOB[n]	62.12	5.30	3.81	62.12	5.26	3.74

[a] Calcd: B, 1.05. Found: B, 1.31. [b] Calcd: for 4:1 dye/borate: water. [c] Calcd: B, 0.90. Found: B, 0.93. [d] Calcd for 2:1:1 dye/borate:water:acetonitrile. [e] Calcd for 6:4:1 dye/borate:water: acetonitrile. [f] Calcd: B, 1.48. Found: B, 1.46. [g] Calcd for 4:1:1 dye/borate:water:acetonitrile. [h] Calcd for 3:2 dye/borate:water. [i] Calcd for 2:3 dye/borate:water. [j] Calcd for 3:1 dye/borate:acetonitrile. [k] Calcd for 3:2 dye/borate:acetonitrile. [l] Calcd for 2:1 dye/borate: acetonitrile. [m] Calcd for 4:4:1 dye/borate:water:acetonitrile. [n] Calcd for 1:1 dye/borate:acetonitrile. [o] Calcd for 4:3 dye/borate:acetonitrile.

$C_{29}H_{34}NB$: C, 85.50; H, 8.41; N, 3.44; B, 2.65. Found: C, 85.14; H, 8.64; N, 3.55; B, 2.72.

9-(*p*-Bromophenyl)triptycene. The triptycene product was prepared from the reaction of benzyne with 9-(4′-bromophenyl)anthracene. The latter was prepared from (4-bromophenyl)lithium and anthrone in ether–benzene solvent.[38] (*p*-Bromophenyl)lithium was prepared in ether at room temperature from 10.0 g (0.0424 mol) of 1,4-dibromobenzene and 17 mL (0.0425 mol) of *b*-butyllithium solution (2.5 M in hexanes). Anthrone in warm benzene was added dropwise and the mixture heated at reflux for 2 h. Water was added and the mixture extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and filtered. Evaporation of solvent gave 7.75 g of solid residue which was chromatographed on alumina to afford 3.1 g of product with 85% purity (60%): ^1H NMR ($CDCl_3$): δ, 8.51 (1 H, s), 8.05 (2 H, d, $J = 8.5$ Hz), 7.72 (2 H, d, $J = 8.3$ Hz), 7.63 (2 H, d, $J = 8.5$ Hz), 7.49–7.44 (2 H, m), 7.39–7.34 (2 H, m) 7.31 (2 H, d, $J = 8.3$ Hz). The bromophenylanthracene was converted to the triptycene by the method of Jefford.[39] (Bromophenyl)anthracene (1,45 g, 4.35 mmol) and 0.9 mL of isoamyl nitrite dissolved in 12 mL of diglyme were heated at gentle reflux. Anthranilic acid (2.0 g. 14.5 mmol) in 10 mL of isoamyl nitrite was added dropwise. Half of the acid solution was added over a period of 20 min. The reaction mixture was cooled, and another 0.9 mL of isoamyl nitrite was added. The solution was heated again at gentle reflux, and the addition of anthranilic acid solution continued. After the addition was complete, the mixture was heated at reflux for 10 min. The mixture was cooled, 5 mL of EtOH was added, and the dark reaction mixture was added to an aqueous solution of NaOH (2 g in 20 mL of water). After the mixture was cooled in an ice bath, a precipitate formed which was isolated by filtration and washed with a cold $MeOH-H_2O$ solution. The solid was filtered through a short column of silica gel and then treated with maleic anhydride in refluxing diglyme for 1 h. After workup as described above and recrystallization from ethanol, 0.592 g of white solid was obtained (33%): ^1H NMR ($CDCl_3$) δ 8.00 (2 H, d, $J = 8.6$ Hz), 7.78 (2 H, d, $J = 8.6$ Hz), 7.43 (3 H, d, $J = 6.6$ Hz), 7.20 (3 H, d, $J = 7.3$ Hz), 7.03–6.92 (6 H, m), 5.42 (1 H, s).

Synthesis of Cyanine Borates. Equimolar amounts of the borate anion, as its tetramethylammonium salt, and the dye cation, as its halide salt, were dissolved in hot acetonitrile. Water was added to the hot solution until a precipitate formed and was slow to disappear. The solution was protected from light and cooled slowly. The resulting crystals were collected by vacuum filtration. The crystals are typically needles and sometimes plates, and the majority have a golden, metallic shine. In some instances, the dye borate precipitates as an oil with the above procedure. In these cases, crystals were obtained by using an equal volume of acetone, acetonitrile, methanol, and ethanol in place of pure acetonitrile. The product purity was determined by NMR spectroscopy and by elemental analysis. The NMR spectra were recorded in acetonitrile solution and are identical with the dye and borate spectra taken individually. Due to the large amount of free space in the borate, solvent is sometimes incorporated in the cyanine borate crystals and can be observed by both NMR spectroscopy and X-ray analysis.[21] Thus, the elemental analyses sometimes incorporated solvent of crystallization. The calculated and observed values are listed in Table 8.

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